Chapter 3
Biomass Conversion to Fuel (Solid, Liquid and Gas Fuel)

Suzana Yusup, Murni Melati Ahmad, Anita Ramli, Khan Zakir, and Mas Fatiha Mohamad

Abstract This chapter highlights the potential of utilising biomass as a renewable feedstock to produce biofuel and biochemical. Technologies for the conversion processes are discussed. In addition, case study on biomass conversion to H_2 is presented. The effect of steam and newly developed bimetallic catalyst (Fe/Ni/Zeolite-β) on palm oil wastes including palm shell (PS) and palm oil fronds (POF) decomposition for H_2 production was experimentally investigated in thermogravimetric analysis-gas chromatography (TGA-GC). Presence of steam increased the H_2 content by 28% for both palm oil wastes. Maximum H_2 content in the product gas generated was 64 mol% from PS for the catalytic steam gasification. On the other hand, for POF maximum H_2 content of 50-mol% is observed in the product gas. Palm wastes can be a potential feedstock for H_2 production utilising catalytic steam gasification process and can contribute to considerable renewable and clean energy for future.

Keywords Biomass conversion • Fuel • Solid • Liquid • Gaseous

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3.1 Introduction

Energy is a fundamental enabler of the economy. The challenges to come are vast utilisation of renewable energy; at the same time the sources of the renewable energy should avoid food versus fuel crisis. This prompted diversity of primary raw materials for manufacturing renewable transportation fuel that includes waste and recycled materials. Table 3.1 shows the relative importance of solid fuels where industrialisation was founded largely on fuels (Tillman 1991). Total fuel consumption is about 76.4 quad.Btu in which biomass is the secondary source to coal as the feedstock. In Malaysia, biomass contributes about 0.5% of fuel used to support the industrial sector (Evald and Majidi 2003).

3.2 Solid Fuel

Biomass is densified into pellets, briquettes, chips, logs and bales in order for it to be utilised as solid fuel. In this form, the mass per unit volume of biomass is increased, thus improving its transportation capacity and efficient storage. The challenge in utilising biomass as solid fuel is to reduce its moisture content, to increase its energy density per volume and to reduce biomass loss due to fragmentation. Incorrect evaluation of its mechanical and physical property will lead to higher transportation cost, higher compacting pressure and additive content. Typical densification process variables are temperature, pressure and pressure application rate, holding time and die geometry (Zachry Engineering Corporation 2009).

Table 3.1 Consumption of coal and biomass fuels in US 1860–1985 (Tillman 1991)

	Fuel consumption (quad.Btu[a])		
Year	Biomass	Coal	Total US energy use
1860	2.6	0.5	3.1
1870	2.9	1.0	4.0
1880	2.9	2.0	5.0
1890	2.5	4.1	7.1
1900	2.0	6.8	9.6
1910	1.9	12.7	16.6
1920	1.6	15.5	21.3
1930	1.5	13.6	23.3
1940	1.4	12.5	25.0
1950	1.2	12.9	35.2
1960	0.8	10.1	44.6
1970	1.0	12.7	67.1
1980	2.4	15.4	78.2
1985	2.5	17.5	76.4

[a] Quadrillion Btu × 1.05 = Exajoule (EJ)

Conditioning of biomass through pretreatment process by chemical, biological or thermal methods helps to improve its property to be utilised as solid fuel. To produce a fuel briquette, inflammable material is pressed under high pressure in a briquette press. Briquetting uses a reciprocating ram or piston to force the ground material through a tapered die. The produced briquettes can be in the form of pucks, logs, etc. of varying diameters and thickness depending upon the equipment and selected die geometry. Roll press briquetting is a well-established technology for the densification of powdery granular materials such as minerals, food products, detergent, coal and sludge (Plistil et al. 2005). Through briquetting, higher energy per volume and uniformity of size and shape is achievable. Proper storage of these solids fuel is crucial since they are moisture sensitive. In addition, solid fuel will emit great amount of smoke at early combustion stage due to high volatile matter content, which led to losses of un-burnt fuel gas (da Rocha 2006). Torrefaction and briquetting will improve the energy content of the solid fuel and is able to overcome the said disadvantages. Briquette is suitable to be used as fuel for boiler having capacity larger than 500 kW. Among the referred standards for wood briquette are Austrian ONORM M 7135 and German DIN 51731. Specifications of solid fuel referred to the standards include chemically untreated biomass, moisture must be <10 wt%, particle density 1–1.09 kg/dm^3, diameter in the range of 25–125 mm and length range is 50–400 mm, ash content on dry matter basis <0.7 wt%, additives <2 wt% and net calorific value is 16.9 MJ/kg (Alakangas et al. 2006).

For pelleting raw materials and pellet processing, the produced pellets must meet similar criteria as briquette with fines must be <2 wt%, diameter of 6 mm and length of five times the diameter and sulphur to be <0.05 wt% of dry matter. For usage in screw feeder boilers, wood chips used are originated from stem wood; moisture is <20–30 wt% with net calorific value of more than 900 kW/bulk m^3.

3.3 Liquid Fuel

Industrialised countries used hardwood biomass to manufacture several chemicals and products since late 1930s. One example is the Ford Plant, in which the hardwood biomass is converted to esters for automotive (Nelson 1930). Plant-based esters can be classified as the green solvents. For an example, glycerol carbonate is used as nonreactive diluents in epoxy or polyurethane systems and 2 ethylhexyl lactate can be used as degreaser and as green solvent in agrochemical formulation. Biomass can be converted to liquid through pyrolysis. Recent advancement in pyrolysis allows shorter heating time, i.e. <2 s at intermediate temperature of 400–600°C in oxygen-free condition. The produced liquid is known as bio-oil and is dark in colour, with energy density of 20 GJ/m^3 and transferrable using exiting oil tankers. It is used as boilers fuels and in specialty chemicals flavouring and colouring. Bio-oil can be upgraded using H_2 or in catalytic environment it can be converted to BTX, MTBE and compatible transportation fuel (Klass 1998).

For ethanol production via fermentation, three types of biomass are employed. They are originated from sugar, starchy and lignocellulosic crops. For sugar crops, pretreatment is unnecessary, but for other crops the cell walls must be disrupted to expose the sugar polymers. The processes involved in ethanol production are pretreatment, hydrolysis and fermentation and product separation through distillation. Contrarily, for direct biomass liquefaction, the biomass is not subjected to heat directly (Klass 1998). Direct liquefaction of biomass is in development stage and, namely, biomass-water slurry process, biomass-recycle oil slurries and hydroiodic acid. In recycled oil slurries, it requires sodium carbonate and CO gas at 250–450°C with 10–30 MPa pressure for conversion to liquid fuel with heating value of 33–34 MJ/kg. For the other process hyroiodic fluid is introduced at 127°C to form hydrocarbon at 60–70% yield. Hew et al. (2010) studied conversion of EFB into liquid product. The EFB-derived pyrolysis oil (bio-oil) is converted to liquid fuel, following Taguchi method. From the analysis, the optimum operating condition for the heterogeneous catalytic cracking process is at 400°C, 15 min of reaction time using 30 g of catalyst weight.

In 1900, Rudolf Diesel demonstrated a direct injection diesel engine fuelled with peanut oil. Ester-type biodiesel is produced catalytically from methanol or ethanol transesterification of triglycerides to methyl or ethyl esters. Its yield and purity depend on ratio of alcohol and triglycerides, catalyst type, temperature and purity of triglyceride. Modhar et al. (2010) investigated the blending of crude palm/crude rubber seed oil and their conversion to biodiesel. Optimum reaction conditions were determined and the conversion of methyl esters exceeded 98%. Biodiesel can be produced from low cost nonedible oils and fats. However most of these sources are of high free fatty acid content which requires two stage processes. The acid treatment step is usually followed by base transesterification since the later can yield higher conversions of methyl esters at shorter reaction time.

3.4 Gaseous Fuel

Biomass can be converted to gaseous fuel through gasification and supercritical water gasification process by means of thermal methods. Various gasifying agents such as oxygen, air or steam can be utilised. The supercritical water gasification process occurs at temperature more than 374°C and 220 atm. This process is suitable for biomass with moisture content more than 50%. Product gas comprised of H_2, CO, CO_2 and CH_4. The formation of tar and char is less with gasification efficiency of almost 100%. This technology is still in developing stage (Kelly-Yong et al. 2007). Typical gasifier is suitable for biomass with moisture content <30%. Operating condition is around 800–900°C and at atmospheric pressure. Various types of gasifier configuration can be found industrially. Examples are for fixed bed with either downdraft or updraft mode of contacting, and for fluidised bed system, the flow behaviour is either bubbling or circulating mode (Hofbauer et al. 2003). Recent advancement in this area is introduction of Absorption Enhance Reforming

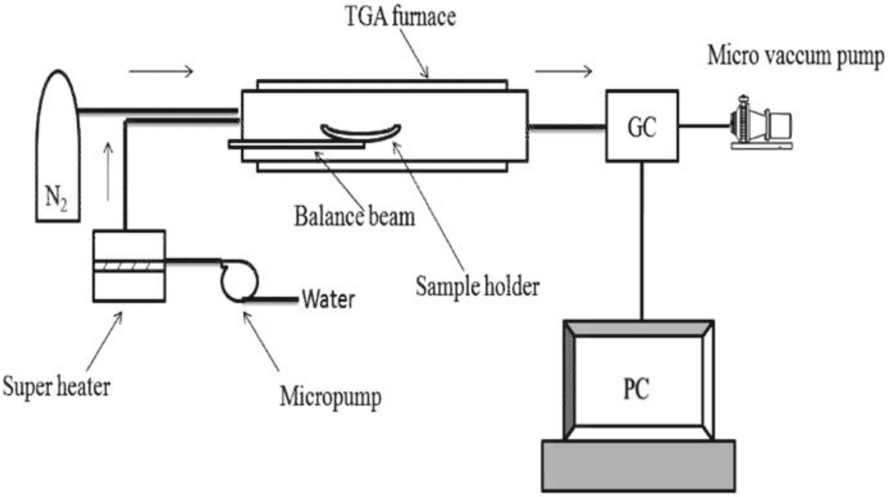

Fig. 3.1 Schematic diagram of lab-scale steam gasification system

that is able to produce hydrogen-rich gas using in situ CO_2 sorbent. In addition, Khan et al. (2011a, b) have investigated the effect of steam and catalyst on palm oil wastes using in situ catalytic adsorption for conversion to H_2. The maximum H_2 content obtained is up to 64 mol% for palm shell, and utilisation of steam as gasifying agent has increased H_2 content by 28%, and further increased in H_2 content by 12.5% is observed when catalyst is introduced to the system. The following paragraph highlights a case study for H_2 production from oil palm biomass.

The biomass steam gasification experiments were performed in a standard TGA (EXSTAR TG/DTA 6300, from SII) and GC (Agilent 7890A, Agilent Technologies) under non-isothermal conditions as shown in Fig. 3.1. For all experiments, biomass sample weight was ~5 mg. N_2 was used as inert carrier gas with a constant flow rate of 100 ml/min.

The micro vacuum pump (650 mmHg was applied throughout the experiments) was attached to the GC to facilitate gaseous product from TGA. Super heater up to 400°C generated steam prior to injection in TGA. The system was purged with N_2 gas (100 ml/min) for about 20 min to remove entrapped gases at temperature of 50°C. All samples were heated at a constant heating rate of 20°C/min from 50 to 900°C where it was kept constant for 10 min. To avoid condensation, steam was introduced when temperature inside the TGA reached to 110°C. The amount of catalyst used was based on biomass-to-catalyst ratio of 3 (mass basis), while steam-to-biomass was kept constant at 1 to 1 ratio (mass basis).

Figure 3.2 shows biomass sample weight % (TG %) and its first derivative (DTG) against temperature range of 200–900°C at a heating rate of 20°C/min (Khan et al. 2011b). Sample drying usually takes place at temperature >200°C which is not

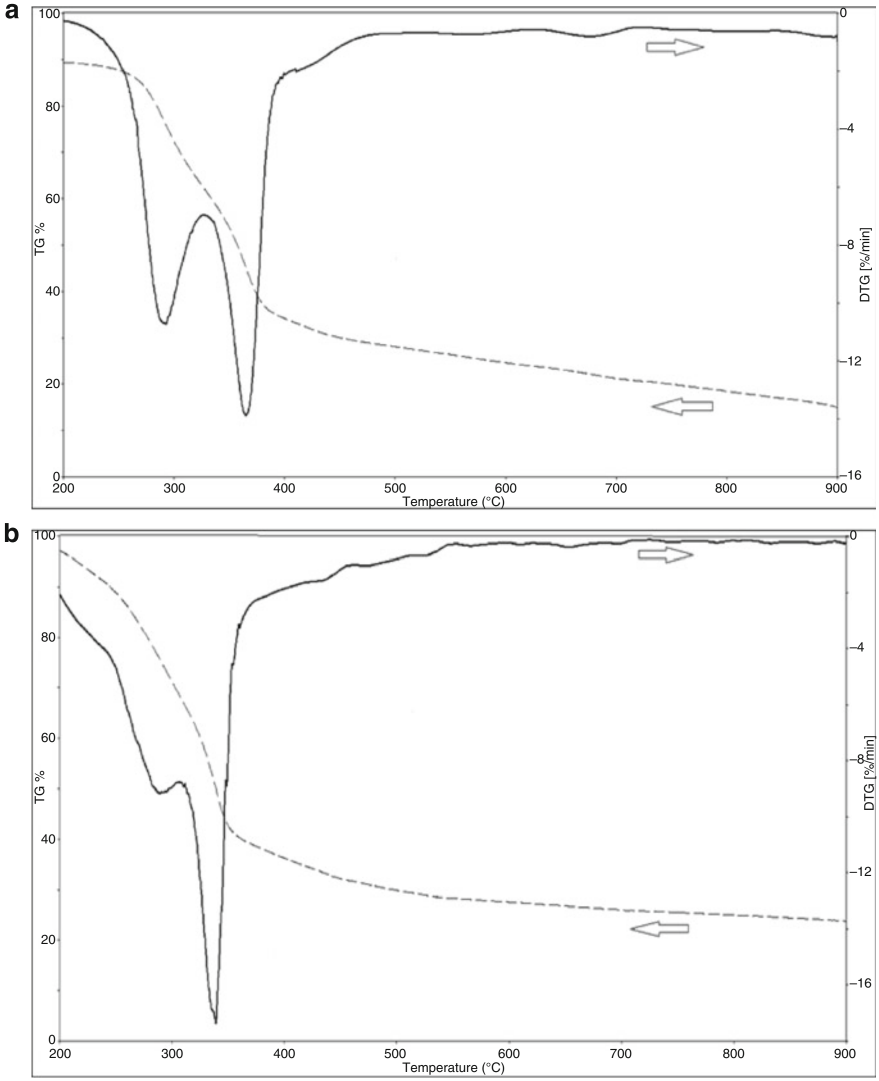

Fig. 3.2 (**a**) TG and DTG curves of palm shell. (**b**) TG and DTG curves of palm oil frond

shown here. In TG curves, the residual fractions for palm shell and palm oil frond were 15% and 24%, respectively.

It is known that lignocelluloses biomass mainly consists of hemicellulose, cellulose and lignin. In biomass thermal decomposition, hemicellulose is first to decompose followed by cellulose, and lignin is the last to decompose due to its heavy cross-link molecules (Yang et al. 2004). Based on this fact, the derivative thermogravimetric (DTG) profiles (Fig. 3.2) for thermal decomposition of PS and POF mainly consist of two dominant peaks appearing at ~300°C and ~340–360°C, respectively. The first peaks represent hemicelluloses decomposition while the second peaks show higher decomposition rate and represent cellulose decomposition.

Based on the profiles, hemicellulose decomposition occurs almost at the same temperature region for both biomass wastes, while cellulose decomposition in PS occurred at higher temperature due to different chemical compositions among the palm oil wastes. In addition, no significant lignin decomposition was observed at 360–900°C that is consistent with findings observed by other researchers (Yang et al. 2004). Figure 3.2 showed the product gas distribution for palm oil frond and palm shell thermal decomposition under inert atmosphere in the absence of steam.

In the present study, H_2 released was mainly observed at temperature range of 450–850°C which is well supported by the results from Seo et al. (2010). Maximum H_2 content was generated at temperature >650°C for PS which was consistent with the literature. On other hand, for palm oil fronds (POF) H_2 content is 19 mol% which was further increased to 34 mol% at 610°C. PS thermal decomposition produced high CH_4 content as compared to POF which may be due to different chemical compositions. In addition, PS gave high H_2 content (40 mol%) particularly at high temperature (690°C) which was due to the high lignin content.

The addition of steam had increased H_2 content in product gas for both palm oil wastes as shown in the Fig. 3.3a, b. (Khan et al. 2011a). Maximum H_2 content for PS and POF were increased from 40 to 56 mol% and 34 to 47 mol%, respectively.

The product gas profiles in catalytic steam gasification of palm oil wastes were shown in Figs. 3.4 and 3.5 (Khan et al. 2011a). The highest H_2 content of 64 mol% and 50 mol% was produced from catalytic steam gasification of PS and POF, respectively (Fig. 3.6a, b). Furthermore, addition of steam had increased H_2 content by 28% for both palm oil wastes, while catalyst addition in steam gasification further increased H_2 content by 12.5% and 6%, respectively, for PS and POF. Based on the data presented, steam contributed significantly to increase the H_2 content in palm oil wastes where newly developed bimetallic catalyst addition gave suitable contribution to H_2 content in product gas particularly for PS.

3.5 Conclusion

Conversion of biomass to fuel and chemical is feasible for small-scale production. The challenge lies on technology deployed at commercial scale with attractive cost. Biomass utilisation reduces the dependency on fossil-based fuel, thus helping to prolong the fuel supply and at the same time reducing the environmental issues related to CO_2 emission since the net CO_2 emission is zero if the fuel source is from biomass.

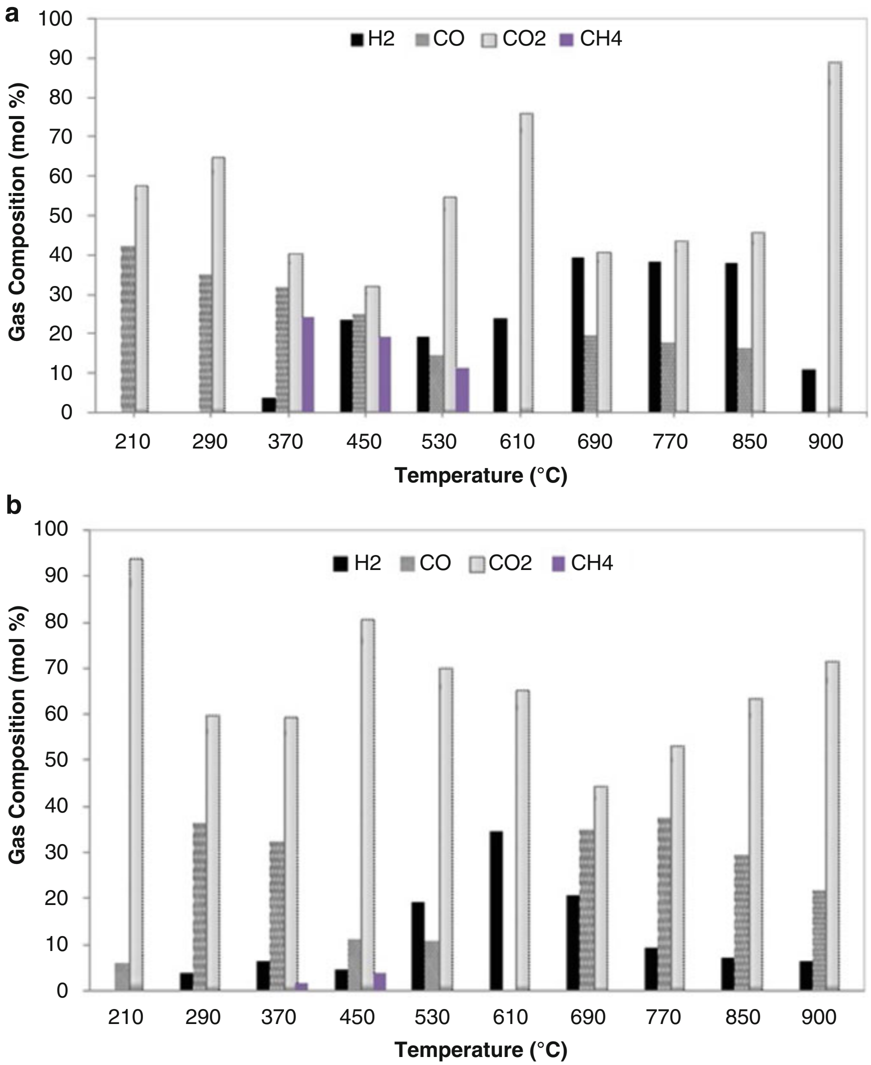

Fig. 3.3 Product gas profiles for thermal decomposition of (**a**) PS and (**b**) POF at inert atmosphere (no steam)

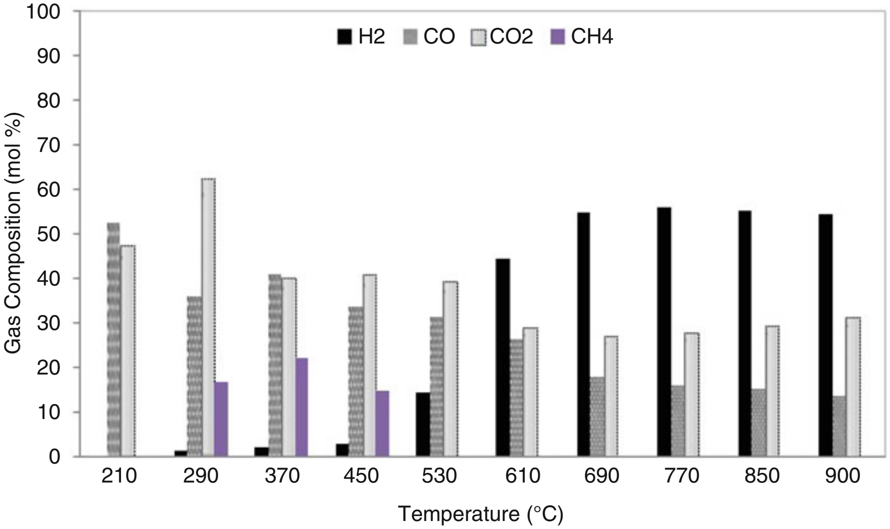

Fig. 3.4 Gaseous profile for PS in steam gasification

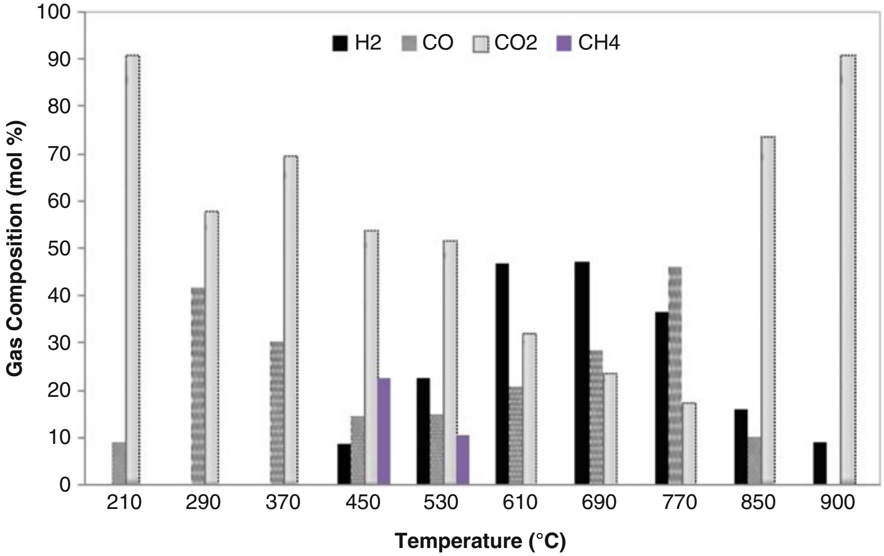

Fig. 3.5 Gaseous profile for POF in steam gasification

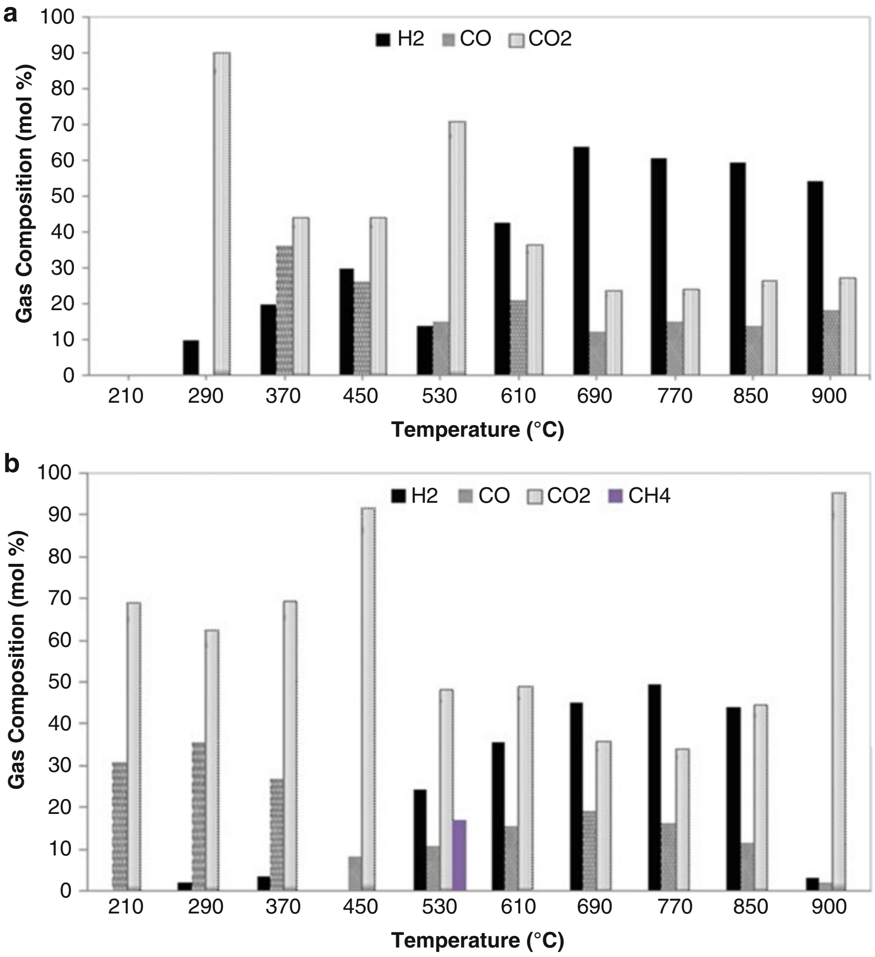

Fig. 3.6 Gaseous profiles of (**a**) PS and (**b**) POF in catalytic steam gasification

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